Preparation of nitrogen doped ZnO thin films by colloidal route

Arnaud Valour, François Cheviré, Franck Tessier, Fabien Grasset, Stéphane Jobic, Laurent Cario, Eric Faulques, Tengfei Jiang

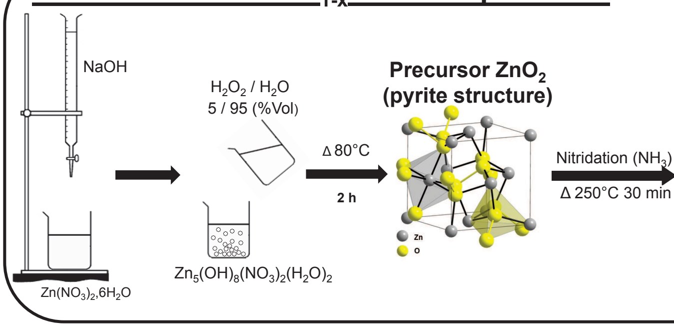
Preparation of nitrogen doped ZnO thin films by colloidal route

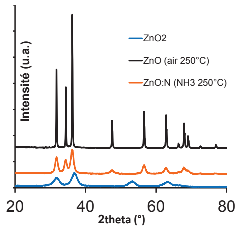
Arnaud Valour [a], François Cheviré [a], Franck Tessier [a], Fabien Grasset [b], Stéphane Jobic [c], Laurent Cario [c], Eric Faulques [c], Tengfei Jiang [c]

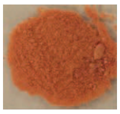
a) Institut des Sciences Chimiques de Rennes (UMR CNRS 6226) – Université de Rennes 1 – France
b) Laboratory for Innovative Key Materials and Structures – National Institute of Material Science (UMI 3629 CNRS/Saint Gobain) – Tsukuba, Japon
c) Institut des Matériaux Jean Rouxel (UMR CNRS 6502) – Université de Nantes – Nantes, France

Zinc oxide is a material of great interest exhibiting pigmental, photocatalytic, piezoelectric, antibacterial, or varistor properties that have already been developed in many different fields of industry. Still novel applications emerge in various domains but they often require the preliminary stabilization of a p-type ZnO counterpart to the natural n-type ZnO to be stimulated. In optoelectronics for instance, the high optical transparency of ZnO thin films coupled with their high electrical conductivity and their strong room temperature luminescence could indeed open up the door to revolutionary technologies as transparent electrodes in solar cells and flat panel displays, light emitting diodes, lasers, etc. We have previously reported the stabilization of p-type nitrogen doped $Zn_{1-x}O$ nanoparticles (ZnO:N) obtained through the decomposition of zinc peroxide (ZnO_2) at low temperature under ammonia flow. Our objective is now to extend these results to the realization of p-type ZnO thin films by colloidal route in order to achieve n-ZnO/p-ZnO:N homojonctions which would led to various applications in optoelectronics. The aim of the present work is to prepare nitrogen doped $Zn_{1-x}O$ thin film by thermal decomposition of ZnO_2 films obtained by chemical conversion of ZnO colloidal thin films.

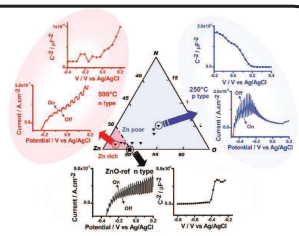
Previous work on $Zn_{1-x}O$:N nanoparticles:





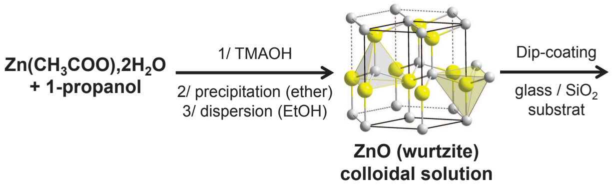


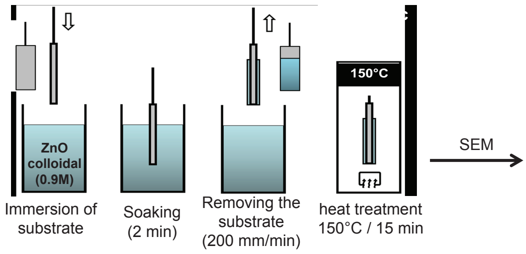
- XRD: ZnO-wurtzite structure type
- Salmon color → nitrogen insertion
- **Material with up to 20% Zn vacancies**
- P-type conductivity stable over more than 2 years



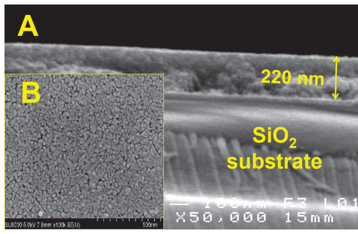
Electrochemical (Mott-Schottky) and photoelectrochemical characterization of ZnO:N prepared at 250°C (blue ellipse), 550°C (red ellipse), and ZnO-ref (gray ellipse). The comparison with the ternary phase diagram reporting the compositions of all compounds suggests that ZnO poor nitrogen-doped samples are p-type while Zn-rich samples are n-type (on = under illumination, off = in the dark).

ZnO thin film synthesis by dip-coating:





→Thickness can be modulate by:
- **Withdrawal speed**
- **Concentration and viscosity of the solution**



SEM:

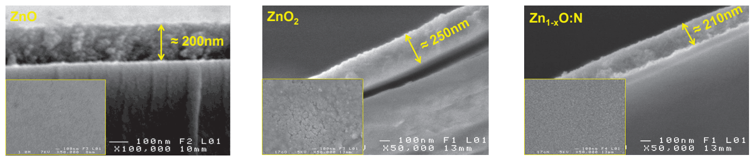
- **A/ regular thickness of ZnO thin film (220nm)**
- **B/ dense and homogeneous ZnO thin film surface with small grain size (<10nm)**

ZnO thin film conversion into ZnO_2 and $Zn_{1-x}O$:N :

$$\text{ZnO thin film} \xrightarrow[H_2O_2 / H_2O \ (5/35\ mL)]{\text{Chemical conversion}} ZnO_2 \text{ thin film} \xrightarrow[\Delta\ 250°C\ 30\ min]{\text{Nitridation under } NH_3} Zn_{1-x}O\text{:N thin film}$$

(slightly orange)

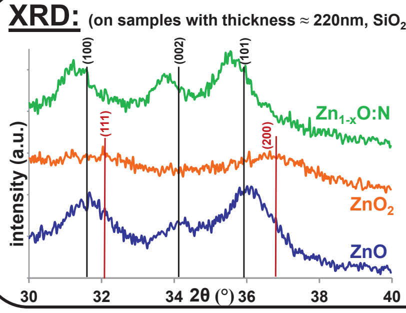
(SEM images of ZnO converted thin films, glass substrate)



SEM:

- **variation of the thickness after conversion in H_2O_2 solution and nitridation**
- **dense and homogeneous surface with increased of grain size after conversion (H_2O_2)**

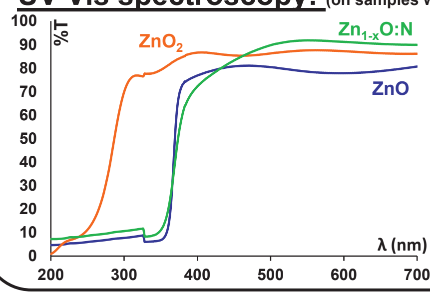
XRD: (on samples with thickness ≈ 220nm, SiO_2 substrate)



XRD :

- **3 ZnO characteristic peaks in the 30°< 2θ < 40° area for ZnO thin film**
- **Conversion into H_2O_2 solution leads to the presence of the two less intense ZnO_2 characteristic peaks**
- **After nitridation, $Zn_{1-x}O$:N thin film with more cristallized ZnO characteristic peaks**

UV-Vis spectroscopy: (on samples with thickness ≈ 220nm, SiO_2 substrate)



UV-Vis :

- **ZnO characteristic absorption band at 370 nm**
- **ZnO_2 absorption band at around 285 nm**
- **$Zn_{1-x}O$:N with two absorption bands: 370 nm (ZnO) and around 450 nm (Nitrogen doping)**

References:

P-type nitrogen doped ZnO nanoparticles stable under ambient conditions.
B. Chavillon, L. Cario, A. Renaud, F. Tessier, F. Cheviré, M. Boujtita, Y. Pellegrin, E. Blart, A. Smeigh, L. Hammarström, F. Odobel, S. Jobic
J. Amer. Chem. Soc. **134** (2012) 464-470

Unravelling the origin of the giant Zn deficiency in wurtzite type ZnO nanoparticles
A. Renaud; L. Cario; X. Rocquefelte; P. Deniard; E. Gautron; E. Faulques; F. Chevire, F. Tessier; S. Jobic
Scientific Reports (2015) submitted

Conclusions:

- **decomposition of ZnO_2 under NH_3 at T=250°C leads to Zn-poor ZnO:N. Zinc vacancy coupled with insertion of nitrogen is necessary to access p-typeness**
- **stabilization of homogeneous, regular and dense wurtzite ZnO thin film by dip-coating (thickness ≈ 200nm).**
- **conversion of ZnO thin film into ZnO_2 by a simple chemical conversion (into H_2O_2 solution) in order to obtain $Zn_{1-x}O$:N films by nitridation under NH_3 at T=250°C**